Association Behavior of Polyoxyethylene (20) Cetyl Ether (Brij 58) and Polyoxyethylene (20) Sorbitan Monooleate (Tween 80) with Polyoxyethylene (4) Lauryl Ether (Brij 30)

A.L. Tan, C.R. Laili, S. Hamdan and S.H. Doreen Ng

Department of Chemical Sciences, Faculty of Science and Technology, University Malaysia Terengganu, 21030, Kuala Terengganu, Terengganu, Malaysia

*Corresponding email: hamdans@umt.edu.my

Abstract

The association behaviour of Brij 58-H$_2$O and Tween 80-H$_2$O with a third component consisting of Brij 30 was investigated. The results were presented in the form of ternary phase equilibriums of H$_2$O - Brij 30 - Brij 58 system and H$_2$O - Brij 30 - Tween 80 systems. The liquid crystalline phase is determined by visual observation of the birefringence under the crossed polarized light. The results showed that the solubilisation for the mixture of Brij 30-Brij 58 and Brij 30-Tween 80 were favourable. The associated formation of self-assembled structures like micelles and lyotropic liquid crystalline were observed. The result showed that the presence of Brij 58 promotes formation of lamellar liquid crystal compared to the Tween 80 counterpart.

Keywords: Ternary phase equilibrium, non-ionic surfactant, isotropic dispersion, liquid crystalline.
1. INTRODUCTION

Surfactants are one of the mostly used chemicals in industrial as well as in daily life. Due to the absence of non-complicated interactions between the counterions and head groups which is not possible in ionic system. Due to these uniqueness, non-ionic surfactants had received a great amount of attention especially in the pharmaceutical, cosmetic and toiletry products area. Furthermore, the growing environmental awareness had also stimulated the search of non-toxic and biodegradable surfactants. More specifically, the surfactant’s behaviours in aqueous solution, particularly how the surfactant interacts with the solvent to form the self-assembled structures we observed, have captured many attentions. Surfactant - H₂O - Oil systems have been widely studied in order to have a better understanding in their structural formations, phase stability, self-assembly process and etc. Surfactants are characterized by their adsorption ability at the surface and interface. In aqueous solution, their prevalence in various structures formation and phase types are based on their composition.

At low concentration in an aqueous solution, the surfactant monomers pack together at the surface or the interface forming a monolayer to lower the surface or interfacial tension. However, as the surfactant concentration increases, the surfactant monomers begin to accumulate as the available area for adsorption reduces. Because the hydrophobic group of the surfactant has very low solubility in the aqueous phase and the hydrophilic group of the surfactant has very low solubility in the non-polar phase, the surfactant monomers are driven by the hydrophobic effect to form self-assembled aggregates. The self-organized aggregates begins with the formation of spherical micelles with aggregation number in the region of 50% to 100% of aqueous phase content by weight, producing an isotropic solution (L₁ phase) with rather low viscosity. As the surfactant concentration increased, the spherical micelles will transform into cylindrical micelles that are anisotropic though the solution still appears as a single phase. However, at much higher surfactant concentration, a series of mesomorphic phases also referred to as liquid crystalline phases will appear. Such liquid crystals that were brought about by the influence of surfactant and solvent were known as lyotropic liquid crystals. Like all liquid crystal, lyotropic liquid crystalline phase exhibits some of the order properties found in crystalline solid and some of the disorder existed in liquids. In general, lyotropic liquid crystalline exists in various forms and structures depending on the type and concentration of surfactant as well as the solvent used.

More than often, because the mixture of surfactants often exhibit synergism and had a better performance than the parent surfactant; mixed surfactants were preferred in formulations and practical application. Theoretically, in terms of performance, the mixtures often have better solubilisation capacity, improved surface activity, lower CMC, improved rheology and etc. Since there was a growing interest on the performance of non-ionic surfactant in H₂O, it is thought that a study on the phase behaviour of the binary mixture of non-ionic surfactant, namely Brij 58 and Tween 80 with Brij 30 in H₂O will provide useful information, especially in the cosmetic and pharmacological formulation area. Both Brij 30 and Brij 58 were from the family of ethoxylated...
fatty alcohol non-ionic surfactant whereas Tween 80 was in the family of ethoxylated sorbitan ester non-ionic surfactant. The regions in which association structures form in H$_2$O will be determined. The results will be presented in the form of triangular diagram of the usual type. In the diagram, the water apex situated at the lower left tip denotes 100% water by weight, while the lower right apex denotes 100% the third component, which in this case is either Brij 58 or Tween 80, and the upper apex denotes 100% of Brij 30.

2. METHODS

2.1. Material

The non-ionic surfactant, polyoxyethylene (4) lauryl ether (Brij 30) (>99%), polyoxyethylene (20) cetyl ether (Brij 58) (99.5%) and polyoxyethylene (20) sorbitan monooleate (Tween 80) (>99%) were purchased from Fluka. The Hydrophilic-Lipophilic Balance (HLB) value and the molecular structure of the surfactants were shown in Table 1. All components were used directly without further purification. Doubly distilled H$_2$O was used as the aqueous phase throughout the study.

2.2. Construction of ternary phase equilibrium

The phase equilibrium was determined by titration to turbidity for the solution part of the system. The samples were then vortexed for mixing purpose. The samples were allowed to equilibrate in a H$_2$O bath kept at 30˚C. The phases were separated by means of centrifugation at high speed.

For the phase diagram, the solutions that are observed as clear and isotropic are identified as one phase micro-emulsion region, whereas for the solutions that are of visibly cloudy dispersions under visual observation are grouped as two phase coarse emulsions. And as for liquid crystal region, the solutions must show birefringence under the crossed polarized light as illustrated in Figure 1.

3. RESULTS AND DISCUSSION

3.1. H$_2$O - Brij 30 - Brij 58 System

The phase equilibrium as presented in Figure 2 showed that the system exhibited the properties of a typical diagram consisting of single ionic surfactant – co-surfactant - H$_2$O components, in which association structures of isotropic dispersions and liquid crystalline can be found in the system. Along the H$_2$O-free axis, it is found that Brij 30 was not miscible with Brij 58. At the Brij 30 apex, it showed that the surfactant was able to solubilised H$_2$O up to 13% by weight, whereas in the Brij 58 apex, H$_2$O
solubilisation only occurred at the H$_2$O content between 8 and 12% by weight. Moving towards the H$_2$O apex, the binary mixtures of Brij 30 and Brij 58 at any compositions were able to form isotropic dispersion at the H$_2$O content between 2 and 12%. As the addition of H$_2$O continued, the isotropic region was in equilibrium with liquid crystalline regions. Thus, resulting the formation of a narrow canal-like pathway of two-phase area.

The next association behaviour observed was the formation of lyotropic liquid crystalline of lamellar type along the Brij 58-free-axis. The mesophase region was observed between 20 and 50% of Brij 30. The region that extended toward the Brij 58 apex, covering a rather large area in the diagram, with a maximum solubility of Brij 58 close to 65%. The formation of lamellar liquid crystalline in this region was consistent and agreed with several studies$^{11-13}$, in which similar liquid crystalline structure was situated at the exact location in other phase equilibrium containing Brij 30 and H$_2$O. When compared with previous studies, it is found that with a different third component, the size of the lamellar liquid crystalline region changes. Apart from the formation of lamellar liquid crystalline, another lyotropic liquid crystalline of hexagonal type was also found along the H$_2$O-Brij 58 axis between 23 and 50% of Brij 58. This region expanded its boundary towards the Brij 30 apex, with the maximum solubility of Brij 30 of 15% and maximum solubility of H$_2$O of 60%. As the H$_2$O content increased slightly, cubic liquid crystalline was formed in the range between 51% and 80% of the total water content. However, the existence of the cubic liquid crystalline was restricted within the area where the composition of Brij 30 not exceeding 3%.

Finally, along the H$_2$O-Brij 58 axis, when the H$_2$O content increased gradually beyond 50% towards the H$_2$O apex, the hexagonal liquid crystalline region had transformed into another association structure of isotropic dispersion with the formation of micellar aggregates. This region covered the area along the H$_2$O-Brij 58 axis, between 75% and 100% of H$_2$O by weight and solubilised 13% of Brij 30. The results were consistent with a previous work by Jacques and co-worker (2008)$^{14}$ but in the H$_2$O - Heptanoic Acid - Brij 58 system.

### 3.2. H$_2$O - Brij 30 - Tween 80 System

By substituting Brij 58 with Tween 80 as the third component, the second phase equilibrium was constructed as depicted in Figure 3. The system exhibited similar trend as observed in system containing Brij 58. The system started out with the formation of isotropic dispersion at both of the Brij 30 and Tween 80 apex with the maximum solubility of H$_2$O of 13% and 22% by weight, respectively. Along the H$_2$O free axis, it showed that Brij 30 and Tween 80 were completely miscible with each other, even in the absence of H$_2$O. The binary mixture of both surfactants at any composition solubilised H$_2$O up to 11% by weight at a lower content of Tween 80. However, at higher content of Tween 80, the amount of H$_2$O solubilised was increased up to about 35% by weight.

Along the Brij 30-H$_2$O axis, as the H$_2$O content increased gradually beyond 13%, the isotropic region was in equilibrium with the liquid crystalline structure. At the H$_2$O content
between 20% and 30%, lamellar liquid crystalline was formed. The region had expanded its boundary toward the Tween 80 apex, with maximum solubilisation of Tween 80 up to 50%. In addition, hexagonal liquid crystalline was found along the Tween 80-H$_2$O axis, in between 37% and 42% of Tween 80 with the maximum solubilisation of Brij 30 up to 5%. The formation was agreed with two previous works which had constructed similar phase equilibriums using soybean oil$^5$ and hexane$^6$ as third component. However, the size of the area differed from one another as the molecular size of the third component changes. Since, hexane had the smallest molecular structure; the hexane-containing system exhibited the largest region. Meanwhile, Brij 30 which had a longer alkyl chain than hexane resulted a smaller area. Eventually, soybean oil which had more complicated molecular structure had the smallest region of all.

Followed by that was the formation of another isotropic region at the Tween 80-H$_2$O axis. The formation occurred at the H$_2$O content of 56% and extended toward the H$_2$O apex. The region projected from the H$_2$O apex towards the H$_2$O free axis with a maximum solubility of Brij 30 of 3%. The formation of isotropic dispersion at this part of the phase equilibrium showed some inconsistency and consistency with three previous works employing the same surfactant but different third component. There was no isotropic region observed when soybean oil$^5$ was used as third component. When soybean oil was replaced by hexane$^6$, monolaurin$^2$ and trioxyethylene alkyl ether$^1$, this isotropic dispersion existed. This is obvious since soybean oil has a larger molecular structure compared to the others. Consequently, it had increased the stearic hindrance between the surfactant. Thus, the formation of micelle was not possible when soybean oil was used.

### 3.3. Brij 58 and Tween 80 Phase Equilibriums Comparisons

When both phase equilibriums were compared, the obvious difference was the size of the liquid crystalline region as shown in Figure 4. The liquid crystalline region had shrunk significantly when Brij 58 was replaced by Tween 80. This great reduction of area was probably due to the difference in molecular structure of Brij 58 and Tween 80 as tabulated Table 1. Brij 58 had straight chain hydrocarbons with 20 ethylene oxide groups attached to the alkyl whereas Tween 80 had a branched structure with 20 ethylene oxide groups scattered between the branches. Being a straight chain in nature allowed Brij 58 to align the molecule side by side without great repulsion to form the neat lamellar phase. In the case of Tween 80, the head group was too large and branching nature of its hydrocarbon parts causing too much stearic hindrance. As a result, it is more difficult to form the lamellar neat phase even though both of them have the similar number of ethylene oxide group. Besides that, cubic liquid crystalline was not found in the Tween 80 system either.

In terms of isotropic dispersion region as illustrated in Figure 5, there was no drastically changing in this region except in the relative size of the region. Similarly, this phenomenon was due to molecular structure of the surfactants. Tween 80 had a branched head group with the ethylene oxide groups spread between the branches. Thus, this enabled the ethylene oxide groups to have larger surface area to interact with H$_2$O. However, in the case of Brij 58, having a straight chain
structure had limited the molecule’s interaction surface area with the H$_2$O, hence reducing its solubility in H$_2$O. Brij 30 with smaller and shorter molecule coexisted in between the Tween 80 molecules to facilitate the formation of the micellar aggregation.

**CONCLUSION**

From this study, it is found that the miscibility of both the mixtures of Brij 58 and Tween 80 with Brij 30 are favourable forming association behaviours typical of H$_2$O-surfactant-cosurfactant. This was expected as non-ionic surfactants are known to mix ideally amongst each. Both of the systems were able to form isotropic dispersion and liquid crystalline structure in the presence of H$_2$O.

**REFERENCES**


**Table 1.** The Hydrophilic-Lipophilic Balance value and molecular structure of the surfactants.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>HLB\textsubscript{Ba} Value</th>
<th>Molecular Structure &amp; Formula</th>
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<tbody>
<tr>
<td>Brij 30</td>
<td>9.7</td>
<td>([C_{12}H_{25}(OCH_2CH_2)OH])</td>
</tr>
<tr>
<td>Brij 58</td>
<td>15.7</td>
<td>([C_{16}H_{35}(OCH_2CH_2)_{20}OH])</td>
</tr>
<tr>
<td>Tween 80</td>
<td>15.0</td>
<td>([C_{24}H_{46}O_6(OCH_2CH_2)_{w+x+y+z}\text{ where } w+x+y+z = 20])</td>
</tr>
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\(\text{a Hydrophilic-Lipophilic Balance}\)
Figure 1. Isotropic solution (Left) and Liquid Crystalline (Right) under crossed polarized light.
Figure 2. The phase equilibrium of H$_2$O - Brij 30 - Brij 58 system.
Figure 3. The phase equilibrium of H$_2$O - Brij 30 - Tween 80 system.
Figure 4. The changes on the liquid crystalline region from the Brij 58 and Tween 80 phase equilibriums.
Figure 5. The changes on the isotropic region from the Brij 58 and Tween 80 phase equilibriums.